GOVERNMENT - INDUSTRY CONFERENCE COMMITTEE REPORTS

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GOVERNMENT-INDUSTRY CONFERENCE ON AIRBORNE RADIOIODINE
C.A. Burchsted
M.W. First, Chairman

GOVERNMENT-INDUSTRY CONFERENCE ON CONTROL OF TRITIUM EFFLUENTS
L.E. Trevorrow
J. Dempsey, Chairman

A third conference committee report in this series entitled:
GOVERNMENT-INDUSTRY MEETING ON FILTERS, MEDIA AND MEDIA TESTING
W.L. Anderson

appears as Paper 7-12 on page 641

GOVERNMENT-INDUSTRY CONFERENCE ON AIRBORNE RADIOIODINE

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The Working Group on Airborne Radioiodine met at AEC Headquarters on March 28, 1974. Dr. Alex Perge gave the introduction for the Division of Waste Management and Transportation, noting the Commission hopes that private industry will take a bigger share in the future in funding and initiating needed research; that there should be a greater effort in the direction of reducing the quantity of material that becomes contaminated as an avenue toward reducing the airborne radioiodine problem, and toward reducing the waste generated to a form suitable for direct storage; and that the Commission must ensure valid bases for future regulations governing airborne releases and contamination.

Dr. First discussed the background of the review committee and its outgrowth from the earlier organization meeting. He noted that its function will be the coordination of efforts concerned with the radioiodine problem and the dissemination of information and research data. A major objective of this meeting was to identify subjects for discussion at the Government-Industry Conference of Adsorbers and Adsorbents which will be held in conjunction with the 13th AEC Air Cleaning Conference in August. Mr. Dempsey noted that the gaseous effluent program had been inherited by WMT from the Division of Operational Safety, and that an important function of these continuing meetings of the Working Group will be to guide WMT in the expenditure of funds and assignment of research related to the radioiodine problem.

Several researchers reported the current status of their projects:

R. A. Lorenz, Oak Ridge National Laboratory. Lorenz is conducting an investigation of charcoal ignition as a possible result of activity loading under accident conditions. He noted that when about 1000 Ci are loaded on a 2-inch by 1-inch diameter charcoal bed that there is a movement of iodine within the bed, even at low temperatures; indication of oxidation above 200°C; and finally a rapid increase in temperature indicating ignition. Although negligible desorption of iodine was observed, it was noted that the tests were terminated as soon as the rapid temperature increase was observed, and that continued combustion would, of course, result in essentially complete desorption of any iodine trapped in the charcoal or added as an impregnant; approximately 0.001% to 1% of the iodine desorbed under the conditions of the three ignition tests performed. He also noted that the CHAR computer program correlates fairly well with experimental results. Next year he plans to conduct tests under high moisture conditions. To date the activity-loading/ignition tests have been made with two coconut-base and one petroleum-base charcoal; future tests of TEDA/KI-impregnated carbons, with added moisture and/or methane, will be made. A question was raised concerning the ignitability of different batches of the same grade of material, and of different samples taken from the same batch.

There have been indications that variations from batch to batch do result in varying ignition characteristics, but no batch-to-batch tests are planned to verify this. There are also plans for bench-scale experiments to measure iodine desorption under closely controlled temperature conditions.

Earl Bennett, United Nuclear Industries. Bennett is conducting engineering-scale aging and weathering tests at the N-Reactor at Richland, Washington, in an effort to obtain comparative data from several charcoal configurations (i.e., impregnant, base material) of the effect of operating environment on weathering, aging, and methyl-iodide performance. Tests are being made with 1-inch thick, pleated-bed (AACC Type I) adsorber cells. Curves showing the results of two different exposure conditions are attached. In test series No. 1, chemical analyses of the samples showed organic pollution of the carbon on the order of 30 mg per g of charcoal, due apparently from a single event cause; subsequent samples taken from the same system after replacement of the charcoal showed a substantially lower degree of poisoning (Series No. 2). Photos of the sample assemblies were shown. Sampling and testing at 6-month intervals will be continued up to a total exposure of at least 24 months as part of the routine quality assurance program of the system. Reports of the program have been issued as DUN-7985 (June 1972) and UNI-39 (July 1973).

A. G. Evans, Savannah River Laboratory. Evans is conducting tests on the performance of charcoals (for radioiodine) in a high radiation field with concurrent exposure to hydrocarbons, moisture, and other adverse environment conditions. Although TEDA-impregnated carbons initially showed the best performance, high TEDA content substantially reduces the ignition temperature (boiling point = 180°C, flash point = 190°C). For Savannah River Plant applications it has been decided to adopt a 1% TEDA, 2% KI impregnation in place of the high level (5%) TEDA impregnation of the charcoals used in earlier tests. SRL observes the same batch-to-batch variations discussed earlier in the meeting, and are conducting tests to identify possible causes for such variations. It is believed that the high temperature thermal desorption test of RDT M 16-1 (June 1972) and recently proposed to ASTM D-28 will provide an effective screening mechanism that can reduce the degree of variation. Analysis of the chemical contents of various charcoal samples showed a wide variation in the potassium:iodine (K:I) ratio which correlated closely with iodine penetrations on a semi-log scale. It was found that better correlation could be obtained by plotting I/K(pH) vs. the log of percent iodine released at 180°C.

Evans noted that the high temperature thermal desorption test is valid even for charcoals which ostensibly will never be exposed to high temperature. There is something present in atmospheric air (at least the air at SRL) which reduces the moisture resistance of the HEPA filters installed upstream of the charcoal adsorbers, which could cause the filters to plug under accident conditions and subsequently reducing airflow and increasing relative to performance of charcoal; development of an NO_x test for aging; effect of sulfur on performance; and other factors affecting performance. Evans stressed that one must consider the trade-offs available in selection of an optimum carbon and pointed out the importance of analyzing the total ventilation system.

Evans also reported on the status of tests to establish the effect of DOP on activated carbon. Naval Research Laboratory exposed samples of carbon to extremely high concentrations of DOP, then the samples were tested by SRL in the radiation exposure test loop. There was no observable difference between the penetration of exposed-to-DOP samples and the nonexposed samples by I_2 or CH_3I. Burchsted noted that the carbon samples were exposed to aerosol DOP, which may not reflect conditions where DOP is impinged on HEPA filters, then desorbs and passes to the adsorbers in the gas phase. It was mentioned that Regulatory Guide 1.52 now calls for bypassing of the DOP around the charcoal beds during in-place testing of HEPA filters.

Victor Dietz, Naval Research Laboratory. NRL is trying to identify the catalytic processes that are operative in the trapping of methyl iodide. It was noted that the conditions encountered in the reactor application are most unfavorable relative to most operations with commercial carbon adsorbents - a very short stay time, very low concentrations, high temperatures and high humidity, all compounded by the radiation environment. The criteria identified at NRL for a successful adsorbent-impregnant system are (1) high efficiency in trapping iodine and organic iodides under the adverse conditions noted, (2) economic competitiveness with currently used activated carbon systems, (3) good thermal stability of the impregnated system, and (4) an acceptable ignition point for the adsorbent system.

NRL is investigating amines other than TEDA of possible interest and has sought the assistance of Armak Chemicals Division as one of the most knowledgeable suppliers. In a recent trip to England, Dr. Deitz visited the Windscale Works and discussed the iodine trapping problem with J. J. Hillary. The laboratory had not been active in studies of iodide trapping since the work reported at the 9th AEC Air Cleaning Conference, but are now starting a new program with the close cooperation of Sutcliff Speakman Charcoals.

Other supports than charcoal are being considered at NRL. These include exfoliated graphites (lower surface area than carbon adsorbents, but more readily impregnated and having a higher ignition temperature), hydrophobic coatings to repel moisture, anchoring of suitable amines on carbon by means of very thin flame-retardant epoxy films. He also suggested that we should look into the information generated during the development of protective coatings for reactor containment structures (see ANSI N.5.9 and N 101.2) as a possible source of data concerning effective iodine traps.

NRL has also been investigating the pre-ignition properties of charcoals as a possible indication of both thermal stability and weathering/aging. The evaluation of carbon monoxide is used as the index and the concentration is recorded by the new Beckman Carbon Monoxide Analyzer. They plan to investigate the effect of bed depth and other factors which may influence the pre-ignition properties of charcoal in service and to obtain comparative data on different carbon-impregnant systems of interest. Dr. Deitz expressed the opinion that the pre-ignition properties may be as significant as ignition itself, but believes this study should be correlated closely with that of Evans and Lorenz.

Dallas Pence, Allied Chemical Corp., Idaho. Allied is beginning the investigation of adsorbents for fuel processing applications, where ^{129}I is the isotope of major concern. They are looking mostly at inorganics such as Ag-zeolites. These are

noncombustible and can be taken to higher temperatures to enchance the reaction. Such materials give particular promise for use in ventilation system serving high temperature operations such as calcining. Allied is investigating properties, performance, and operational characteristics of these materials. They are also investigating amine-impregnated inorganic catalyst supports, and believe that the higher amines will give substantially higher ignition temperatures than TEDA. Allied is looking at the longer range picture of ultimate collection and storage of iodine. It is expected that a fuel processing operation will produce about 250 to 300 g ^{129}I per ton of fuel, 200 g of which might be in the offgas -- this must be collected and stored. Large-scale testing of promising materials may eventually be conducted in the air cleaning system of the Idaho Chemical Plant.

G. O. Wood, Los Alamos. Wood reported that Los Alamos is primarily concerned with adsorbents for air sampling and are just getting into the business. He noted that they had observed considerable lot-to-lot variation in activated carbons earlier, but that more uniform materials are now being received. Several attendees questioned the latter conclusion, however. Wood stressed the need for a simple, rapid procedure for testing batches of charcoal.

Kovach, Pence, and Evans stated that the nuclear industry is experiencing considerable lot-to-lot variation in activated carbons received from the same manufacturer, and considerable grade-to-grade variation among carbons from different manufacturers. There is also considerable experience with poor loading and installation of samplers, particularly in commercial nuclear power plants.

J. L. Kovach, Nuclear Consulting Services. Kovach observed that the background of stable iodine in the atmosphere is not being considered in air sampling and in airborne iodine standards. The variation in concentration appears to be less than 5 ppm from coast to coast, and the concentration itself is much greater than the values being considered as "low" (see discussion below). For accurate testing, this background iodine must be removed; Kovach suggests removing the carbon from the samplers (as supplied), leaching it with NH_3OH, and then reloading the sample canister properly.

Kovach advocates the use of sacrificial "guard" beds for adsorber systems (as earlier recommended by Burchsted, par. 3.4.3, ORNL-NSIC-65).

He suggests the use of tritium-tagged methyl iodide for field testing of adsorber systems. It gives a more sensitive test and avoids problems arising from Freons in the atmosphere (Freons are frequently used for cleaning, dye-penetrant inspection of welds, and halogen leak detection) which tend to "blind" the Freon-leak-test. The tritium-tagged methyl iodide is fast (2 to 3 sec. penetration), requires only small amounts of activity (about 1/10 microcurie per cubic meter of air), and does not "blind" the bed so that scanning can be effective. The technique is not applicable to PWR in-containment systems, however, because, of the high neutron fields encountered.

Round Table Discussion

Pence. We need guidance on Regulatory requirements for input to the ANSI standards for radioiodine testing of adsorbents. We need to know what future systems will be like (ANSI N45-8 is now assuming that in-containment ESF adsorber systems

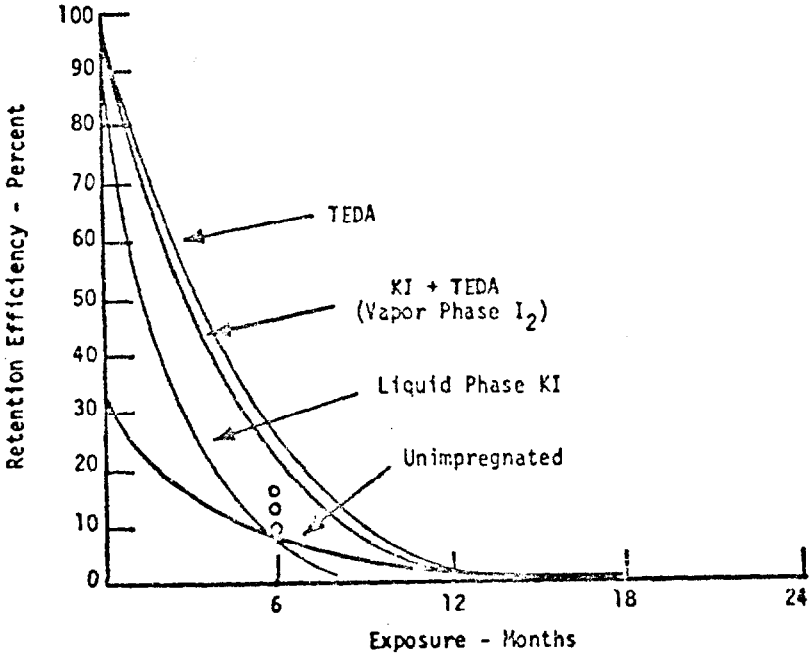
are passe) and what accident, normal, and fuel-processing environments we should simulate in our testing, and what iodine species we should assume. Normal radwaste offgas system costs are going from the $100 K's level to the $1000 K's level, so it is important to establish assumptions for the guidance of design. Evans noted that it is important to define the behaviors of iodine at low concentration, but that we must also define "low". Collins suggested a value of 10^{-10} to 10^{-13} microcuries/cc. Kovach noted again that this is substantially below normal iodine background; the value may be valid for concentration immediately downstream from the adsorber, but is not reasonable for concentrations external to the plant itself. Kovach also noted that tests to date with various isotopes showed no significant differences and questioned the practice of defining "low" on an isotope-by-isotope basis for any concentration below background.

First noted that an objective of the committee is to obtain and disseminate information from all sources. However, as Benaroya pointed out, it is normal practice in the commercial reactor business (including utilities, vendors, and architect engineers) to keep tests made by or for the utility proprietary -- Regulatory has no method of releasing the information furnished to them in answer to questions. A main thrust in the Carbon-Industry Conference to be held in conjunction with the 13th AEC Air Cleaning Conference in August should be to promote the free exchange of information and data. It is essential to get these people together to convince them that the proprietary information approach is self-defeating.

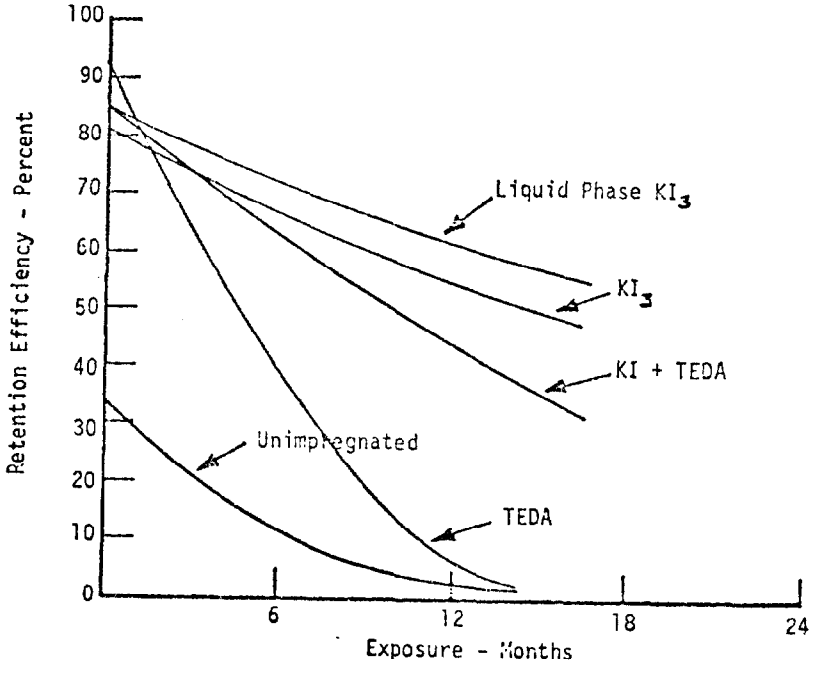
Zavadoski noted that Regulatory needs an identification and quantification of environmental poisoning of adsorbents; he plans visits to commercial reactors to identify some of these factors. Other problems that may have to be considered in the future are co-adsorption of Br, I_2, Cs, Rh, and other volatiles in the environment. Kovach mentioned the corrosion problem with Type 304-L stainless steel which is becoming evident in commercial reactors. Other cell materials, perhaps Type 316 stainless steel, may have to be considered. It is already known that coated carbon steel is inadequate, however. Pence noted the need for more definitive qualification of test personnel. Burchsted noted a potential supply problem in the growing consumption of activated carbon and the concurrent recognition of limited life. Burchsted reported that the domestic carbon survey is being reactivated.

After some discussion, First requested the attendees of the meeting to consider and advise him on whether to keep the Government-Industry Conference in August a closed meeting or to open it up to all who wish to attend. Two suggestions were made, one to have the invited attendees at the table and chairs around the room for others; the second to invite open attendance but with a maximum of one or two from any one organization. Items which might be included on the agenda of the G-I Conference are:

1. Fire extinguishment and prevention -- I:C ratios to prevent ignition.
2. Acceptable deluge system design. Administrative controls.
3. Need for a central test and evaluation facility ("Wilhelm rig").
4. A thorough review and evaluation of currently available adsorption data.



METHYL IODIDE RETENTION OF
WEATHERED IMPREGNATED CHARCOALS



METHYL IODIDE RETENTION OF
WEATHERED IMPREGNATED CHARCOALS

IODINE ADSORPTION REVIEW COMMITTEE MEETING
MARCH 28,1974

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GOVERNMENT-INDUSTRY CONFERENCE ON CONTROL OF TRITIUM EFFLUENTS

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The primary objective of this conference was to discuss techniques that might eventually be developed to the point of commercial application if collection and retention of tritium from the light-water reactor fuel cycle becomes mandatory. Attention was focused on the ultimate disposition of low-level aqueous wastes (LLAW), the expected carrier of the major fraction of tritium in the light-water reactor fuel cycle. The discussions included a number of alternative disposal procedures that might be adopted in the event that future regulations prohibit the vaporization of LLAW into the atmosphere. The alternatives were grouped into two major categories; those that included an isotope-separation process, resulting in a concentrate to be stored and a depleted stream to be either dispersed or recycled as make-up water to the fuel-reprocessing plant, and those which do not contain an isotope-separation step.

Each presentation by the persons named below was open to discussion by any of the 44 persons who attended this conference. Since much of the work described is in progress, results are not reported here in detail.

Fixation in Solids

P. Colombo (Brookhaven National Laboratory) reported on development of techniques to fix tritiated water in two types of solids, polystyrene-impregnated concrete and polyacetylene. The first process is carried out by making a concrete from tritiated water and either Portland cement or a high-alumina cement, then soaking the concrete in polystyrene monomer containing a catalyst to promote subsequent polymerization. The second process involves the reaction of tritiated water with calcium carbide to produce a tritiated calcium hydroxide and a tritiated acetylene which is polymerized by ^{60}Co gamma radiation to a powdered solid. The tritiated calcium hydroxide can be incorporated into concrete, and the polyacetylene may prove to be an acceptable waste form without such incorporation. Rates of tritium leaching have been observed to be low for the polymer-impregnated concrete, and essentially zero for the polyacetylene. The mechanical properties of polymer-impregnated concrete have been observed to be superior to those of ordinary concrete.

Options for Disposal of Germany's Reprocessing Wastes

M. Laser (Institute of Chemical Technology, Kernforschungsanlage, Jülich, Germany) reviewed a number of options for disposal of LLAW including tank storage, injection into exhausted oil fields, sea disposal, and fixation in concrete or plaster. He concluded that shipping of LLAW for disposal into the sea would be the most economic option, if permitted; that onsite solidification would also be

relatively inexpensive and safer; and that, if storage in a salt mine is chosen, then enrichment by distillation followed by solidification would be recommended.

Deep-Well Injection

L. E. Trevorrow (Argonne National Laboratory) reported on an evaluation of deep-well injection of LLAW recently begun at ANL. This technique has been used to solve various waste disposal problems that involved large volumes of liquids. Available information on this technique includes recorded experience in the application to industrial wastes, which has increased greatly in recent years, and early evaluations for high-level radioactive wastes. An initial review of this information resulted in recommendations of categories to be given primary attention in the evaluation of application to LLAW. The categories include resolution of details and updating of information on the location of suitable disposal sites, characterization of LLAW composition in order to permit prediction of the required pre-injection treatment, compilation and clarification of present legal and regulatory constraints, updating of cost estimates, and estimation of environmental risks.

Separation by Extractive Distillation and by Exchange

J. Bixel (Mound Laboratory, Monsanto) described a search for organic solvents that would enhance the separation of tritium from hydrogen in an extractive distillation of water. The search has been conducted by reviewing recorded information on molecular properties and by experimental measurements of vapor-liquid equilibria.

He also described preparations to test the efficiency of a new catalyst, to be supplied by Engelhard Minerals and Chemicals Corp., to promote the exchange between hydrogen and water, a reaction that has been employed in the concentration of heavy water. Unlike catalysts previously employed for this exchange, the new catalyst is purported to be hydrophobic, and capable of operating efficiently in contact with water in the liquid phase. This property would permit simplifications in contact column design, leading to reductions in both capital and operating costs.

Separation by Solvent Effects and by Laser Excitation

L. Burger (Battelle-Pacific Northwest Laboratory) reported on experimental tests to determine the possibilities of hydrogen isotope separation by selective distribution in aqueous-organic systems, both by solvent extraction and by extractive distillation of water.

He also outlined studies in progress of the absorption spectrum of the water molecule in the preparation of a scheme for separation of hydrogen isotopes by selective excitation with a laser.

Separation by Exchange and by Electrolysis

S. Ribnikar (Boris Kidric Institute, Yugoslavia) described recent improvements in catalyst efficiency and column design for concentration of tritium by exchange between hydrogen and water. In this column, exchange takes place at the catalyst-coated interior

surface of the outer tube, liquid water flows down a cylindrical, central surface, and hydrogen flows up through the annular space between these surfaces. This design is expected to offer reductions in both capital and operating costs over the design used in heavy-water production in the plant at Trail, British Columbia. These developments, which originated at the Institute for Stable Isotopes, Cluj, Romania, had been aimed initially at improving D_2O production. Tests at Boris Kidric Institute have confirmed that the new catalyst also shows improved efficiencies for tritium exchange. The group at Cluj has proposed pilot-scale tests on removal of tritium from simulated PWR effluents.

Ribnikar also described plans to test an electrochemical technique, termed reversible electrolysis, which involves electrolysis of water, membrane permeation of the nascent hydrogen, and its immediate recombination with oxygen.

Further, he outlined the thesis that, if isotope separation were used for tritium control, then a scheme that involves partial tritium depletion and recycle of LLAW as aqueous makeup for the fuel-reprocessing plant would require lower separative work and cost than a scheme that involves drastic stripping of the LLAW in order to discharge it to environment.

Separation by Palladium Membrane

E. H. Kobisk (Oak Ridge National Laboratory) described progress in demonstrations of the feasibility of separation based on differences in permeation rates of the gaseous hydrogen isotopes through palladium membranes. Results of permeation measurements were presented for pure hydrogen and pure deuterium. Plans were described for proceeding to work with pure tritium and then with tritium-hydrogen mixtures.

Plans for also beginning an experimental investigation of the reversible electrolysis were briefly stated.

Costs and Benefits in Tritium Control

J. Cohen (Lawrence Livermore Laboratory) presented results of calculations to support the case that cost/benefit values for tritium control, in terms of dollars per man-rem averted, are much higher than for control of ^{85}Kr. Also, the values may be unacceptably higher than values for alternative allocations of the money toward solution of other sociological problems.

W. Carr (Allied-Gulf Nuclear Services) also presented independent considerations questioning the utility of tritium control, including the hazards of storing a concentrated waste, the interpretation of the as-low-as practicable specification for effluents, the time needed for development of a separations process to the point of commercial installation, and the opportunity cost of allocating resources to tritium control.